

"DIRECTIONAL VALENCES"

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I. Two approaches are known for approximately solving any problem of chemical bonds that proposes to determine the direction of valences: the first approach studies the approximate solution for a whole molecule; that is, the so-called method of molecular orbits. The second approach studies the molecule at null-approximation with separate atoms.

This treatise on directional valences has reference to the second method of approach which was first worked out in its fundamentals by Pauling and his school (L. Pauling, I.A.C.S. 53, 1367, 1931; R. Hultgern, Phys.Rev. 40, 891, 1932) and by Kimball (G.E. Kimball, J.ch. Phy. 8, 188, 1940).

Pauling's method consists of seeking the equivalent orthogonal "hybrid" functions whose maximums possess significant values relative to directional chemical bonds. Kimball's method is based on the application of the theory of groups to the study of those symmetrical properties, of mono-electron functions of a central atom, that take part in the formation of the bond. Influencing the formation of both methods was the experimental fact that the valence angles are but slightly dependent upon the kind of combining atoms and, as a consequence, it was assumed that valence directions in a molecule are determined chiefly by the distribution of electrons according to quantum states in a central atom.

Study of the problem from the point of view of separate electrons of a central atom and searches for the optimum hybrid functions for each of the valence directions - these (study and searches) are joined with difficulty, which difficulty arises in consequence of the non-agreement between (a) the number of unknowns that are subject to determination, on the one hand, and (b) the number of conditions to which these unknowns are subjected, on the other hand. In order to determine

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the valence angles it is necessary to draw some supplementary comparisons.

It is possible to avoid the difficulty, if the "hybrid" functions are subjected to stronger conditions than the condition of orthogonality, namely, ["]on the average["], relative to the entire dimension; that is to say, if one requires that each wave-function ψ_g be able to be simultaneously taken by just one electron, as required by Pauli's principle. But in such a case the problem of determining directional valences leads to the polyelectron problem.

We shall take any one of the hybrid functions, let us say, the first:

$$\psi_{g_1} = a_{11}\psi_1(1) + a_{12}\psi_2(1) + \dots + a_{1n}\psi_n(1) \quad (1)$$

In the valence direction N , it should reach a maximum value:

$$\psi'_{g_1} = a_{11}\psi'_1(1) + a_{12}\psi'_2(1) + \dots + a_{1n}\psi'_n(1) = 0 \quad (2)$$

where ψ'_{g_1} is the symbolic expression for the derivative of ψ_{g_1} with respect to the coordinates of the first valence electron.

We require that the state of wave-function ψ_{g_1} has been occupied by just the first electron, which fact can be expressed by the following system of equations⁵:

$$(m-1) \text{ equations } \begin{cases} \psi_{g_1}(2) = a_{11}\psi_1(2) + \dots + a_{1m}\psi_m(2) = 0 \\ \psi_{g_1}(3) = \dots \\ \psi_{g_1}(m) = a_{11}\psi_1(m) + \dots + a_{1m}\psi_m(m) = 0 \end{cases} \quad (2a)$$

The systems of equations similar to systems^{and} (2)₁, (2a)₁, are as many as there are valence electrons. Each of them is a homogeneous system of m equations. Since not all the coefficients a_{1i} are transformed into zero, otherwise the first wave-function would be identically equal to zero, $\psi_{g_1} \equiv 0$, then:

$$\begin{vmatrix} \psi'_1(1) & \psi'_2(1) & \dots & \psi'_m(1) \\ \psi_1(2) & \psi_2(2) & \dots & \psi_m(2) \\ \dots & \dots & \dots & \dots \\ \psi_1(m) & \psi_2(m) & \dots & \psi_m(m) \end{vmatrix} = 0 \quad (3)$$

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Obviously the type of conditions (3) will also be m ; all of them can be written down in compact form if we introduce the function ψ_a :

$$\psi_a = \begin{vmatrix} \psi_1(1) & \psi_2(1) & \cdots & \psi_m(1) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(m) & \psi_2(m) & \cdots & \psi_m(m) \end{vmatrix} \quad (4)$$

Then all $2m$ conditions can be written thus:

$$\frac{\partial \psi_a}{\partial \theta_i} = 0 \text{ and } \frac{\partial \psi_a}{\partial \phi_i} = 0 \quad (i = 1, 2, \dots, m) \quad (5)$$

These equations express the fact that m systems possess non-trivial solutions for coefficients a_{ij} and, consequently, the psi wave-functions $\psi_{g_1}, \psi_{g_2}, \dots, \psi_{g_n}$ obtain significant values different from zero in the direction of chemical bonds. Since, moreover, these equations should be maximums (extremals), then the valence coordinates found from (5) should give the maximum value of the psi wave-function ψ_a .

Therefore, we have arrived at the problem of determiningⁱⁿ the directional valences in a central atom with m valence-electrons of similarly oriented spins, but the arrived-at problem is distinct from previous formulations of it.

Finding the solutions of the equations (5) is comparatively simple, thanks to the great symmetry of the expression (4) and thanks to the convenient form of the spherical functions that permit in many cases the simple geometrical interpretation of the problem. For the purpose of illustration we shall give some very simple examples, 1, 2, 3 below:

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1. Combination of functions $SP_x P_y$. The expression (4) is equal to:

$$\begin{aligned}\psi_a &= \begin{vmatrix} s(1) & p_x(1) & p_y(1) \\ s(2) & p_x(2) & p_y(2) \\ s(3) & p_x(3) & p_y(3) \end{vmatrix} = \sim \begin{vmatrix} 1 & \sin\theta_1 \cdot \cos\phi_1 & \sin\theta_1 \cdot \sin\phi_1 \\ \dots\dots\dots & \dots\dots\dots & \dots\dots\dots \\ 1 & \sin\theta_3 \cdot \cos\phi_3 & \sin\theta_3 \cdot \sin\phi_3 \end{vmatrix} \\ &= \begin{vmatrix} 1 & x_1 & y_1 \\ 1 & x_2 & y_2 \\ 1 & x_3 & y_3 \end{vmatrix} \quad (6)\end{aligned}$$

Coordinates $(x_1, y_1), (x_2, y_2), (x_3, y_3)$ can be considered as projections of the unit vectors:

$$\vec{k}, \vec{l}, \vec{m}$$

which lie in the plane (XY). Expression (6) is proportional to the area of a triangle, which is expressed, as found in analytical geometry, by the coordinates of the three vertices. The area of the triangle will be a maximum when all angles at the vertices equal 120° . The same vectors indicate the directions of the three valences.

2. The following combination below holds:

$$\begin{aligned}\psi_a &= \begin{vmatrix} p_x(1) & p_y(1) & p_z(1) \\ p_x(2) & p_y(2) & p_z(2) \\ p_x(3) & p_y(3) & p_z(3) \end{vmatrix} \cong \begin{vmatrix} \sin\theta_1 \cdot \cos\phi_1 & \sin\theta_1 \cdot \sin\phi_1 & \cos\theta_1 \\ \dots\dots\dots & \dots\dots\dots & \dots\dots\dots \\ \sin\theta_3 \cdot \cos\phi_3 & \sin\theta_3 \cdot \sin\phi_3 & \cos\theta_3 \end{vmatrix} \\ &= \begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} \quad (7)\end{aligned}$$

The requirement that the psi-function ψ_a be a maximum results in the requirement that expression (7), which is proportional to the volume of a parallelepiped expressed through the coordinates of its apices, be a maximum value. The last requirement is met if the angles between the vectors $\vec{k}, \vec{l}, \vec{m}$ are right-angle, 90° .

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3. The combination $s p_x p_y p_z$ gives:

$$\psi_a = \begin{vmatrix} s(1) & p_x(1) & p_y(1) & p_z(1) \\ \dots & \dots & \dots & \dots \\ s(4) & p_x(4) & p_y(4) & p_z(4) \end{vmatrix} \cong \begin{vmatrix} 1 & x_1 & y_1 & z_1 \\ 1 & x_2 & y_2 & z_2 \\ 1 & x_3 & y_3 & z_3 \\ 1 & x_4 & y_4 & z_4 \end{vmatrix} \quad (8)$$

Expression (8) is proportional to the volume of a tetrahedron (pyramid) which is expressed by the coordinates of its apices. The angles between valence directions are tetrahedral.

II. It is possible to arrive immediately at a new formulation for determining the directional valences, without any need to study the hybrid functions.

Since we are determining the valence directions in a "molecule" with separate atoms, then in such an approximation the best that we can do, in the sense of the successively developed idea of the Heitler-London method, is to require that, in these parts of the "tern" molecule where interchange is possible, Pauli's principle be strictly adhered to. It is obvious that the atomic function antisymmetrical in the coordinates of the valence electrons will be the best zero solution for the electrons of the central atom with similarly oriented spins.

The method of hybrid functions uses, as mono-electron functions, only the part that depends on the angular coordinates. From the point of view of the proposed method, such an approach ~~to the~~ solution of the problem is optional and remains true as long as it is possible to ~~use~~ express the atomic psi-function ψ_a (namely:)

$$\psi_a = \begin{vmatrix} \psi_1(1) & \psi_2(1) & \dots & \psi_m(1) \\ \dots & \dots & \dots & \dots \\ \psi_1(m) & \psi_2(m) & \dots & \psi_m(m) \end{vmatrix} \quad (9)$$

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as a product of two separate functions thus:

$$\psi_a = R(r) \cdot K(\theta\phi)$$

Here $\psi_1, \psi_2, \dots, \psi_m$ are the full mono-electron functions, including the radial dependence (that is, they are functions of the radius r).

We shall use the approximate functions of Slater:

$$\psi_i = N \cdot r^{n^*-1} \cdot e^{-\frac{Z^*}{n^*} r_i} \cdot K(\theta_i \phi_i)$$

where: N is a normalizing constant

n^* is the effective main quantum-number

Z^* is the effective charge of the nucleus acting on the given electron

r is expressed as radii of the first hydrogen orbit

Since, in (10), Z^* possesses one and the same value for the s and p electrons, but a different value for the d electrons, then it is always possible to effect a division of the variables in the wave-function ψ_a , if either the s and p electrons or the d electrons take part in the combination. In the general case of the spd combinations, it is possible to say anything about the possibility of such a division. Excluding from consideration the radial functions, we can then assume a small difference for the sp and d states; and when we compare the corresponding functions of Slater, we are satisfied with the very approximate character of the assumption. It seems more consistent not to limit the method to postulating the identity of the radial functions for electrons that enter in the bond, but in such a case the determination of the valence directions is placed in dependence upon the physically-reasonable determination of several intra-atomic distances characteristic of the given atom in the given valence state.

Such a statement of the problem can be justified just in that case, if with the help of the resulting radial distance r_{oi} we shall

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be in a position, even if qualitative, to reflect tangibly on the existing inter-atomic distances in the molecule. Unfortunately, it is impossible to reassure ourselves very much in this direction, firstly, because the mono-electronic functions of Slater appear as functions of a free atom - that is, as a null-approximation of the functions of a bound atom; secondly, because the same method of determining inter-atomic distances is based on the empirical law of additivity of co-valence radii that are not always justified actually; and thirdly, because in actually existing molecules, as is right, the bonds do not bear a purely covalent character.

We shall determine the radial distance r_{0i} from the conditions governing the maximum probability of residence of binding electrons as a function of the distance in the given valence-direction; that is, we must demand that the following product

$$\psi_a^2 \cdot r_1^2 \dots r_m^2 \cdot dr_1 \dots dr_m \cdot \sin \theta_{01} \dots \sin \theta_{0m} \cdot d\theta_1 \dots d\theta_m \cdot d\phi_1 \dots d\phi_m \quad (11)$$

be a maximum for any $dr_i, d\theta_i, d\phi_i$. Hence it follows that:

$$\frac{\partial}{\partial r_i} [r_1 r_2 \dots r_m \cdot \psi_a]^2 = 0 \quad (i = 1, 2, \dots, m) \quad (12)$$

If we introduce the function $\Phi = (r_1 r_2 \dots r_m \cdot \psi_a)^2$, then the system of equations following:

$$\frac{\partial \Phi}{\partial r_i} = \frac{\partial \Phi}{\partial \theta_i} = \frac{\partial \Phi}{\partial \phi_i} = 0 \quad (i = 1, 2, \dots, m) \quad (13)$$

uniquely determines m valence directions and m radii of a free atom in the valence -state. Hereafter in contrast to the radii of free atoms in a normal -state, we shall designate them "valence-radii (=radii of a free atom in the valence-state)".

Taken into account ^{here} is the fact that the central atom can possess various "valence-radii" for the various directions. In addition, inasmuch as the central atom can exist in various valence-states (in various molecules),

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then to each state there will correspond a proper collection of valence-radii (see Table 1).

In connection with this, it would be of interest to compare the results of experiments on the structure of the molecules TeCl_4 , PCl_5 and PF_3Cl_2 with the calculated inter-atomic distances (calculated radius of the central atom plus the radius of the joined atom, given in the table). Such a comparison gives the results as shown in Table 2.

Table 2

Author	Molecule	Structure	Bond	Inter-Atomic Distances in Angstroms (Å)	
				Experimental	Calculated
Stevenson & Shomaker (JACS 62, 267, 1940)	TeCl_4	C_{2v}	Te-Cl	$R_z = 3.37$ $R_{xy} = 2.33$	3.04 2.15
M. Rowanlt (C.r. 207, 620, 1938)	PCl_5	Three-Sided Bipyramid	P-Cl	$R_h = 2.25$ $R_A = 2.10$	2.25 1.93
L.O. Brockway & J.V. Beach (JACS 60, 1836, '38)	PF_3Cl_2	Ditto	P-Cl P-F	$R_h = 2.05$ $R_A = 1.59$	2.25 1.68

Table 1

Spatial Disposition of the Bonds

Valence of the Central Atom	Configur- ation of the Bonds	Combin- ing Functions	Radii of the atoms in the valence-state
2	Linear	dp	$r = 2n^{*2} / (Z_s^{*} + Z_d^{*})$
		sp	$r = n^{*2} / Z_s^{*}$
	Angular	p ²	$r = n^{*2} / Z_s^{*}$
		sd	$r = 2n^{*2} / (Z_s^{*} + Z_d^{*})$
3	Symmetrical Planar (Truly Triangular)	d ²	$r = n^{*2} / Z_d^{*}$
		sp ²	$r = n^{*2} / Z_s^{*}$
		p ² d	$r = 3n^{*2} / (2Z_s^{*} + Z_d^{*})$
		d ³	$r = n^{*2} / Z_d^{*}$
	Non-Symm. Triangular Pyramid	d ³ s	$r = 3n^{*2} / (2Z_d^{*} + Z_s^{*})$
		dsp	$r = 3n^{*2} / (2Z_s^{*} + Z_d^{*})$
4	Tetrahedron	d ² p	$r_z = 2n^{*2} / (Z_s^{*} + Z_d^{*})$; $r_x = n^{*2} / Z_d^{*}$
		p ³	$r = n^{*2} / Z_s^{*}$
	Triangular Pyramid with central atom as Base	sp ³	$r = n^{*2} / Z_s^{*}$
		d ³ s	$r_1 \approx r_2 = r_3 = r_4$
		d ³	$r_1 \neq r_2 = r_3 = r_4$

TeCl₄, PCl₅ and PF₃Cl₂ with the calculated inter-atomic distances (calculated radius of the central atom plus the radius of the joined atom, given in the table). Such a comparison gives the results as shown in Table 2.

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L.O. Brockway & I.V. Beach (JACS 60, 1836, '38)	PF ₃ Cl ₂	Ditto	P-Cl P-F	R _h = 2.05 R _Δ = 1.59	2.25 1.68

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		sd	$r = 2n^{*2} / (Z_s^{*} + Z_d^{*})$
		d ²	$r = n^{*2} / Z_d^{*}$
3	Symmetrical	sp ²	$r = n^{*2} / Z_s^{*}$
	Planar	p ² d	$r = 3n^{*2} / (2Z_s^{*} + Z_d^{*})$
	(Truly Triangular)	d ³	$r = n^{*2} / Z_d^{*}$
		d ³ s	$r = 3n^{*2} / (2Z_d^{*} + Z_s^{*})$
	Planar	dsp	$r = 3n^{*2} / (2Z_s^{*} + Z_d^{*})$
	Non-Symm.	d ² p	$r_z = 2n^{*2} / (Z_s^{*} + Z_d^{*})$; $r_x = n^{*2} / Z_d^{*}$
	Triangular Pyramid	p ³	$r = n^{*2} / Z_s^{*}$
4	Tetrahedron	sp ³	$r = n^{*2} / Z_s^{*}$
		d ³ s	$r_1 \approx r_2 = r_3 = r_4$
	Triangular Pyramid with Central Atom as Base	d ³	$r_1 \neq r_2 = r_3 = r_4$
	Distorted Tetrahedron	spd ²	$r_z = n^{*2} / Z_s^{*}$; $r_{\Delta} = 3n^{*2} / (2Z_d^{*} + Z_s^{*})$
		p ³ d	$r_1 \neq r_2 = r_3 = r_4$
	Planar Symm. (Square)	sp ² d	$r = 4n^{*2} / (3Z_s^{*} + Z_d^{*})$
		d ² p ²	$r = 2n^{*2} / (Z_s^{*} + Z_d^{*})$
	45° Angled Pyramid (Central Atom in Apex)	d ⁴	$r = n^{*2} / Z_d^{*}$
		p ³ d	$r = 4n^{*2} / (3Z_s^{*} + Z_d^{*})$
	Structure C _{2v}	p ³ d	$r_z = 2n^{*2} / (Z_s^{*} + Z_d^{*})$; $r_{xy} = n^{*2} / Z_s^{*}$
5	Bi-pyramid	sp ³ d	$r_z \neq r_{\Delta}$
		d ³ sp	$r_z \neq r_{\Delta}$
	45°-angled pyr.	$n^{*2}/2$	$r \neq r$

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4-angled pyr.	sp^3d	
Cent. Atom	d^4s	
within the pyr.	d^2p^3	$r_z \neq r_o$
on its altitude	d^4p	
5-angled pyr.	d^5	$r = n^2/Z_d^*$
Cent. Atom at apex		
Planar True	d^3p^2	$r = 5n^2/(3Z_d^* + 2Z_s^*)$
Pentagon	sp^2d^2	$r = 5n^2/(3Z_s^* + 2Z_d^*)$
6 Octahedron	d^2sp^3	$r = 3n^2/(2Z_s^* + Z_d^*)$
Triangular	d^4sp	$r = 3n^2/(2Z_d^* + Z_s^*)$
Prism	d^5p	$r = 6n^2/(5Z_d^* + Z_s^*)$
Triangular	p^3d^3	$r = 2n^2/(Z_s^* + Z_d^*)$
Anti-Prism		
7 Pentagonal	sp^3d^3	$r_z \neq r_{xy}$
Bipyramid		
8 Square	d^5p^3	$r = 8n^2/(5Z_d^* + 3Z_s^*)$
Anti-Prism	sd^4p^3	$r = 2n^2/(Z_s^* + Z_d^*)$

Experimental data of the table confirms the qualitative conclusions given by us above.

We observe, from Table 1, that in combination p^3d what probably takes place during the formation of molecules like $TeCl_4$ can be three types of valence schemes and stable molecular forms corresponding to them:

- 1) structure ;
- 2) distorted tetrahedron;
- 3) pyramid with the central atom at its apex.

Calculations show that in the last case the atom Te is raised only slightly over the plane of the base and the angle $Cl - Te - Cl$ equals 87° . In combination sp^3d , what takes place in molecules of type PCl_5 can be of two structures:

- 1) structure of triangular bipyramid;
- 2) structure of a quadrangular pyramid with the central atom located within the pyramid on its altitude.

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According to Pauling, the stability of each bond in the molecule can be characterized by the so-called "bond strength"; that is, the maximum value of the binding function in a given valence direction. The method stated here permits use to introduce the quantity which enables us to determine the probability of forming the structure in question; because of this property we can use the following function:

$$\Phi_m = (\Gamma_{01} \cdot \Gamma_{02} \cdot \Gamma_{03} \cdots \Gamma_{0m} \cdot \psi_{a_{max}})^2$$

where $\psi_{a_{max}}$ is the value of the atomic function of valence coordinates $\Gamma_{0i} \Theta_{0i} \phi_{0i}$.

It is of interest to compare the quantity Φ for various structures in combination p^3d and sp^3d . Calculations give for the molecules $TeCl_4$ and PCl_5 :

$$(\text{for } p^3d:) \Phi_{m_{C_{2v}}} : \Phi_{m_{tetra}} : \Phi_{m_{pyr}} = 100 : 25 : 7$$

$$(\text{for } sp^3d:) \Phi_{m_{bipy}} : \Phi_{m_{pyr}} = 100 : 84$$

These data show that the most probable structure of $TeCl_4$ proves to be C_{2v} , but for molecule PCl_5 it is a bipyramid. The results agree with experience.

Conclusion:

1. A method is proposed that permits one to study all-possible combinations of the spd functions and to compare one ~~or~~^{or} several stable binding configurations for each combination.
2. The study of complete mono-electron functions, including the radial part $R(r)$, permits one to make qualitative conclusions regarding the possibility of the presence of various inter-atomic distances for various directions in the molecules with the same joined atoms (PCl_5 , $TeCl_4$, $SeCl_4$ etc), which are formed by a central atom in the valence state: d^2p , d^3s , spd^2 , p^3d , sp^3d and in several others.

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3. The method permits answering the question about which structure is the most probable, if for a given combination of the functions there are several possibilities of stable configurations.

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Submitted
23 July 1947

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